

CHANGES IN THE DEGREE OF SUBSTITUTION
OF PAC FROM PYROLYSIS OF A HIGH VOLATILE BITUMINOUS COAL

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INTRODUCTION

When pyrolyzed, coal forms a complex mixture of polycyclic aromatic compounds (PAC), many of which carry functional groups as substitutes for ring hydrogen. Further subsection of PAC to pyrolytic conditions causes changes in their composition--manifested partly by changes in the degree of substitution. The presence or absence of substituent groups is of importance to environmental issues concerning both the sources of environmental PAC and their health effects. Researchers (22,26,36,45) studying PAC in the air, water, and soil have tried to deduce information about the PAC source fuels and their process temperatures from relative abundances of certain alkylated and unalkylated PAC.

Focussing particularly on alkyl and amino substituents, several researchers (14,18,30,31,32,54) have attempted to establish a link between biological activity (i.e., carcinogenicity or mutagenicity) and the presence or absence of substituent groups. Results to date indicate that biological activity is a complex function of the identity of the parent PAC, the nature of the functional group, the size of the functional group (18,32), and the position of the substitution (2,3,21,33,34,47)--all factors that influence the electron distribution within the compound. It is logical that these factors should also be the ones that govern PAC reactivity under pyrolytic conditions, but a thorough investigation of all of these influences lies beyond the scope of any single work. It is our objective to determine how the degree of substitution and the nature of the substituent groups influence the pyrolysis behavior of coal-derived PAC.

Previous work has already revealed some information about pyrolysis-induced changes in substitution of PAC from coal pyrolysis. Serio (46) has used nuclear magnetic resonance spectroscopy (NMR) to show that increasing pyrolysis severity by either temperature or time effects an increase in aromaticity and a decrease in the presence of functional groups. Employing Fourier transform infrared spectroscopy (FT-IR), Solomon, et al. (50) and Freihaut and Seery (13) report that high temperature coal tar exhibits a considerable reduction (as compared to lower temperature tar) of IR absorption in the regions associated with functional group attachment to aromatic rings. Other researchers (5,25,53) have used gas chromatography-mass spectrometry (GC-MS) to identify some specific alkylated PAC produced in coal pyrolysis experiments. We are unaware of any work to date that reports total mass yields of substituted and unsubstituted PAC from coal pyrolysis.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

To produce the PAC of this study, 44-53 μm particles of PSOC 997, a Pittsburgh Seam high volatile bituminous coal, are fluidized in argon and fed at a rate of 2.5 g/hour into the laminar flow, drop-tube pyrolysis furnace of Figure 1. Details of the furnace appear elsewhere (41). An optical pyrometer is used to measure furnace

temperature, which can be set to values of 1000 K to 2000 K by adjustment of the electrical power input. Particle residence time, or "drop distance," is controlled by adjusting the vertical position of the water-cooled collection probe. As pyrolysis products exit the reaction zone at 5.3 std l/min, they encounter 17.1 std l/min of argon quench gas at the top of the collection probe and another 4.8 std l/min through the walls of the probe inner tube as they travel the length of the collection probe. Leaving the probe, they enter an impactor for size-separation of the solid pyrolysis products. Char particles, the larger of these, deposit on the first stages; aerosols (i.e., PAC-coated soot) end up on the lowest impactor stages and the Millipore teflon filter (hole size, .2 μ m) following the impactor. After passing through the filter, the gases are channeled to infrared detectors for measurement of CO and CO₂ and to a flame ionization detector for measurement of hydrocarbon volatiles. A small portion of gas is diverted to a 750 ml glass bulb for subsequent GC-MS analysis.

After all products are weighed, the aerosols are placed in teflon-capped, 30-ml amber glass bottles of Caledon distilled-in-glass HPLC grade dichloromethane (DCM) and sonicated for five minutes. Syringe-fulls of the particle/liquid suspension are passed through a Millipore teflon filter (hole size .2 μ m) to remove the soot particles from the PAC/DCM solution. The mass of the residue soot is taken and subtracted from that before sonication to give the mass of the PAC. Triplicate 100- μ l aliquots of the PAC/DCM solution are removed, evaporated, and weighed according to the procedure of Lafleur, *et al.* (27) to verify the PAC yields. This latter procedure gives \geq 90% recovery for naphthalene and 100% recovery for species of \geq three rings, so negligible PAC mass is lost during evaporation since, in our experiments, one-ring aromatics and lighter hydrocarbons stay in the gas phase; only aromatics of \geq two rings condense onto the soot.

The PAC/DCM solutions undergo analysis by GC-MS, HPLC, and FT-IR. The GC component of the GC-MS system is a Hewlett-Packard Model 5890, equipped with a Quadrex Super Cap Series, methyl silicone (film thickness .10 μ m) high temperature, aluminum clad capillary column (15 m x .2 mm i.d.). Sample volumes of .1 μ l are introduced into the splitless injector, maintained at 300°C. The detector is kept at 320°C, and the column temperature is programmed from 40°C to 320°C at 10°C/min. The mass spectrometer, Hewlett-Packard Model 5970, operates in electron impact mode at an ionizing voltage of 70 eV. Mass spectra are taken at a frequency of .77 scans/second, over a mass to charge ratio range of 41 to 600.

The HPLC system, fully described elsewhere (28), consists of a Perkin-Elmer Series 4 quaternary solvent delivery system coupled to a Model LC-85B variable wavelength ultraviolet (UV) detector. 1.5 ml/min of DCM (same grade as above) flows through the steric exclusion column (50 cm long x 10 mm i.d.), which is packed with 500 Å Jordi-Gel poly(divinylbenzene). Samples are injected through either a 6- μ l or a 100- μ l Rheodyne injection loop, and a microswitch on the injector actuates the data system to insure reproducible starting times. As demonstrated in another publication (28), substituted PAC elute in the first 23.9 ml; unsubstituted, afterward. The proportions of the UV response areas before and after 23.9 ml are taken to represent respectively the proportions of substituted and unsubstituted PAC. (To alleviate uncertainty about the relative UV response factors for the two classes of PAC, we have collected the eluates before and after 23.9 ml for one sample, concentrated them under nitrogen, and subjected them to the microbalance weighing procedure (27) mentioned above. Because the UV area technique gives good agreement with the weighing procedure, this latter, more time-consuming procedure is unnecessary.)

For FT-IR analysis, drops of the PAC/DCM solutions are placed on KBr discs (20 mm x 2 mm), and the solvent is allowed to evaporate. The discs are placed in an IBM Model IR/32 Fourier Transform Infrared Spectrometer, equipped with a Globar source and a mercury-cadmium telluride detector. The resulting absorbance spectra represent 64 scans, taken at a resolution of 8 cm^{-1} . To insure that the PAC composition is uniform over the surface of the disc, each disc is rotated slightly two times for additional determinations.

RESULTS AND DISCUSSION

Figure 2 displays the yields of soot and PAC collected on the aerosol filter for the two sets of experiments: Set 1, constant drop distance (6 in) and variable temperature, and Set 2, constant temperature (1375 K) and variable drop distance. First, it should be noted that our maximum PAC yield of ~9% lies significantly below the 24-26% primary tar yields obtained from experiments conducted under less severe conditions (7,46). Our maximum PAC yield or "zero point" thus corresponds to a significant degree of primary tar conversion (~65%). Evident from Figure 2 are the drop in PAC yield and the compensating rise in soot yield as pyrolysis conditions increase in severity--by an increase in either temperature or distance. The constancy of the sum of PAC and soot yields ($21.34\% \pm 0.97\%$ for Set 1; $19.86\% \pm 1.09\%$ for Set 2) supports the previously reported notion that PAC serve as precursors to soot (9,17,24,42,52). It should be borne in mind, however, that our experiments and ones done prior to them (41) also show small temperature- and time-induced decreases in the yields of char, CO_2 , and hydrocarbons and an increase in that of CO.

To better understand this apparent transformation of PAC to soot, it is necessary to investigate the compositional changes in the PAC that accompany their conversion. We have chosen to describe compositional changes of the PAC in terms of their aromatic ring number distribution and their degree of functional group substitution. A discussion of changes in the ring number distributions of coal-derived PAC will appear elsewhere (55); this paper focusses on pyrolysis-induced changes in the degree of substitution.

The question of how the degree of substitution changes can be partially answered by the GC-MS total ion chromatograms in Figure 3, featuring PAC from three Set 1 experiments. Since PAC elute in the order of decreasing volatility or of increasing molecular weight, addition of a functional group brings about a small increase in retention time; addition of an aromatic ring, a large increase. Readily apparent from Figure 3 is the loss of compositional complexity as temperature is raised. The lowest temperature sample is comprised of a multitude of peaks, many unresolved, which correspond to unsubstituted PAC and their substituted homologs. As temperature increases, the number of peaks diminishes drastically. Large gaps emerge between clusters of unsubstituted PAC isomers--indicating a marked depletion in the substituted species.

Even though GC-MS can easily give a qualitative picture of substitutional differences in PAC from coal, it is extremely difficult to use GC-MS quantitatively due to the unresolvability of some peaks, the uncertainty of response factors, the limited number of species included in available mass spectra libraries, and the virtual indistinguishability of mass spectra of some isomeric PAC (at least for mass spectra from systems with electron impact ionization sources (6,19,23)). Even if all of these difficulties are surmounted, the usefulness of GC-MS still extends only to the portion of the PAC sample that is gas chromatographable, i.e., to the

vaporizable components. (It should be noted that this vaporization limitation of GC-MS systems promises to soon be eliminated by the introduction of new supercritical fluid chromatography-MS systems (35).)

Unlike GC, HPLC is limited in applicability only by component solubility in the mobile phase; but, except for microcolumn HPLC techniques (43), the price for the wider range of component applicability is the loss of separation efficiency as evident in peak resolution. This "drawback" can be an advantage in analyzing mixtures as complex as fossil fuel products, however, because HPLC methods can be tailored to make bulk separations according to one or two structural parameters. We have recently developed a method with a steric exclusion HPLC column that takes advantage of a nonexclusion effect to separate substituted from unsubstituted PAC (28). Non-nitrogen-containing PAC with alkyl, phenyl, hydroxyl, carbonyl, carboxyl, etheric, esteric, cyano, or nitro functional groups elute as size-excluded species. Unsubstituted PAC are adsorbed onto the column and elute later (28). Nitrogen-containing PAC are also delayed by adsorption unless they have a substituent group that sterically blocks the N atom from the adsorption site (29).

Figure 4 presents the results of applying this technique to the PAC from the two sets of experiments. Yields of substituted PAC fall monotonically with either increasing temperature or drop distance. Over the temperature interval investigated in Set 1, the drop is by two orders of magnitude; over the distance interval in Set 2, the drop is by almost an order of magnitude. Yields of unsubstituted PAC, on the other hand, exhibit a dual behavior. They appear to be insensitive to pyrolysis conditions at temperatures ≤ 1312 K for Set 1 and at distances ≤ 4 inches for Set 2. Beyond these "critical values," however, they too decay with an increase in either temperature or distance. Again the decline is more dramatic for the experiments in Set 1.

The qualitative similarity of the curves in Figure 4a to those in 4b suggests that the data of the two sets of experiments be compared as plots versus a parameter of pyrolysis severity--such as total PAC yield--that accounts for both temperature and time effects. The result of combining Figures 2 and 4 appears in Figure 5, which contains data from Sets 1 and 2 as well as experiments conducted at combinations of temperature and distance not covered by these Sets.

The fact that all the data (to a first approximation) lie on the same lines suggests the following for the ranges of temperature (1125 to 1473 K) and time (approximately .050 to .325 sec particle residence times, corresponding to drop distances of 2 to 6 in) investigated:

- 1) The split between substituted and unsubstituted PAC is solely a function of PAC yield (or conversion) and depends on temperature or time only as much as these variables affect PAC yield (or conversion).
- 2) Since pyrolysis at long time and low temperature can give the same results as at short time and high temperature, the PAC conversion reactions have a narrow distribution of activation energies.
- 3) It is more practical to relate substituted and unsubstituted PAC yields to total yield than to temperature and residence time, quantities whose measurements tend to be more system- and method-dependent.

It is convenient to approximate the S (substituted PAC) and the U (unsubstituted PAC) curves in Figure 5 as two line segments of different slope, intersecting

at a critical PAC yield Y_c , the point after which there is net loss of unsubstituted PAC. The value of Y_c is 4.5 mass% of coal--corresponding to 48% PAC conversion if the point of maximum PAC yield is taken as 0% conversion. Since both S and U must be 0 at $Y = 0$, the equations for the lines can be obtained easily in terms of Y , the total PAC yield:

$$\begin{array}{lll} \text{Regime 1:} & Y > Y_c & U = U_0 \quad S = Y - U_0 \\ \text{Regime 2:} & Y < Y_c & U = (U_0/Y_c)Y \quad S = (1 - U_0/Y_c)Y \end{array}$$

Thus for these experiments, once the critical yield Y_c and the initial yield of unsubstituted PAC U_0 have been experimentally determined, the yields of substituted and unsubstituted PAC can be calculated solely from measurement of Y . The equations imply a ratio of S to U that, in Regime 1, decreases with decreasing Y and, in Regime 2, stays constant. The data match these approximations much better at large Y than at small Y , however, because the relative error of the straight line approximations for S and U becomes greater as Y decreases. Since secondary pyrolytic reactions depend much less on the parent coal than do the primary pyrolytic reactions, one might expect PAC from other coals (especially other bituminous coals) to exhibit the same "two line" behavior of U and S yields (albeit with different values of Y_c and U_0).

The transition from Regime 1 to Regime 2 in Figure 5 suggests a change in the nature of the functional groups associated with the substituted PAC. Figure 6 displays the FT-IR spectra of samples from three Set 1 experiments--each labeled with the functional groups conventionally assigned (4,48) to peaks at particular bands. These spectra appear unretouched, i.e., their baselines have not been "corrected" to screen out the drift allegedly due to scatter (44,49,51). The prominent functional group absorbances occur at 2850-2980 cm^{-1} and 1370-1460 cm^{-1} for alkyl groups; at 3150-3550 cm^{-1} for OH or the NH of amides or amines; at 1260-1280 cm^{-1} for etheric C-O; and at 1690-1730 cm^{-1} for carbonyl groups. The three oxygen-containing groups--hydroxyl, ether, and carbonyl--are the same as those reportedly found in coals of $\geq 80\%$ carbon (1).

Socrates (48) cautions against comparing changes in relative intensities of functional groups' bands to get changes in their relative amounts because signals associated with particular functional groups can be augmented (and sometimes shifted) by certain adjacent atoms or functional groups (e.g., the intensity of the C-H aromatic stretch band at 1600 cm^{-1} can be enhanced by either ring nitrogen or hydroxyl groups (51)). Nevertheless, we can make some qualitative observations from the spectra in Figure 6. Most noticeable is that the OH or NH groups responsible for the 3150-3550 cm^{-1} band in Figure 6a disappear by 1312 K (6c) and remain absent from the spectra of samples produced at higher temperatures. This observation is consistent with the ^1H NMR determination of a temperature-induced drop in hydroxyl content of the bituminous coal tars of Collin, et al. (8). If, as recommended (50), aromatic H is represented by the 700-900 cm^{-1} band and aliphatic, by the 2800-3000 cm^{-1} band, then Figure 6 also reveals a reduction in aliphatic (or hydroaromatic) hydrogen relative to aromatic hydrogen--a reduction consistent with the results of Solomon, et al. (50) for tars of another Pittsburgh Seam bituminous coal. Figure 6 also implies a relative decrease in etheric functionalities and a relative increase in carbonyl functionalities as temperature increases. PAC thus appears to adhere to the following order of reactivity:

hydroxyl- and/or amino-substituted PAC > alkyl- and ether-substituted PAC > unsubstituted PAC and PAC with carbonyl groups.

It is instructive to compare this experimentally observed order of reactivities with what might be predicted from frontier orbital theory. According to this theory (11), the bonding between two reactants participating in any of a number of kinds of reactions (e.g., concerted, free radical, ionic) occurs by overlap of the highest energy occupied molecular orbital (HOMO) of one species with the lowest energy unoccupied orbital (LUMO) of the other. Reactions are most energetically favored for high HOMO energies and low LUMO energies. If the reactant providing the LUMO is fixed, then the reactivities of compounds reacting with this species will follow the order of the compounds' HOMO energies. Except for a minus sign, ionization potentials are "roughly the energies of the HOMOs" (11), so lower ionization potentials denote higher energy HOMOs and higher reactivities. Figure 7 displays the values of ionization potentials, measured by photoionization mass spectrometry, as reported by Franklin, *et al.* (12) for a variety of one- and two-ring PAC. Figures 7a, b, and c show that the reactivity of an aromatic species is increased by an increase in either the number of alkyl substituents or the number of carbons within an alkyl substituent. Figure 7c reveals the strongly activating effect (relative to benzene) of an amino N attached directly to the aromatic ring. Figure 7d shows the activating effect of etheric or hydroxyl groups and the slightly deactivating effect of the carbonyl group. Thus PAC reactivity, as inferred from ionization potentials, follows the order:

aromatic amines > aromatic ethers \approx multialkylated PAC \approx phenols >
 monoalkylated PAC > unsubstituted PAC \geq carbonyl-substituted PAC,

consistent with our experimental observations.

The above order helps to explain the behavior of the S curve in Figure 5. In Regime 1, the substituted PAC are composed of a significant portion of very reactive compounds with hydroxyl and/or NH, etheric, and alkyl functional groups. The S curve falls steeply as these very reactive substituted PAC disappear. By the end of Regime 1, the total mass of substituted species--especially that of the most reactive ones--is severely reduced. The slope of the S curve thus becomes less steep.

Interpretation of the U curve in Figure 5 is less clear-cut. In addition to the values in Figure 7, Franklin, *et al.* (12) provide ionization potentials for some PAC of \geq two rings (e.g., anthracene, 7.55 eV; benzo[c]phenanthrene, 8.12 eV; and acenaphthylene, 8.73 eV), which indicate a variation in reactivity among the unsubstituted PAC as well. Two alternatives emerge to account for the behavior of the U curve.

Alternative 1 holds that there is a significant difference between the reactivities of the unsubstituted PAC and the substituted PAC with the more activating functional groups (amino, hydroxyl, ether, multialkyl). While these highly reactive substituted PAC are present (Regime 1), soot formation is dominated by the conversion of these species. There may be conversion reactions within the unsubstituted PAC class to accommodate differences in individual species' reactivities, but there is negligible transfer into the class from conversion of substituted PAC or out of the class from conversion of unsubstituted PAC to soot in Regime 1. At the end of Regime 1, however, the remaining substituted species are much less reactive than those initially present, and there is no longer a large disparity between the reactivities of the substituted and unsubstituted PAC. The unsubstituted PAC begin to convert to soot too, and the U curve declines in Regime 2.

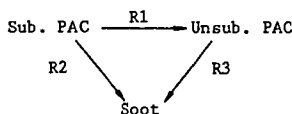
Alternative 2 suggests that, although the substituted PAC are more reactive as a class than the unsubstituted PAC, there are certain unsubstituted PAC with reactivities comparable to those of the more reactive substituted PAC. These more reactive unsubstituted PAC convert to soot in Regime 1, where their loss is offset by a gain in unsubstituted PAC produced by reactions of substituted PAC. As pyrolytic conditions become more severe (Regime 2), conversion of unsubstituted PAC to soot prevails over production of unsubstituted PAC. The balance is upset, and the U curve declines.

The two Alternatives represent fairly extreme cases. It is certainly likely that the true interpretation lies somewhere between these extremes, but our data do not permit us to be any more exact at this time.

The three pronounced peaks between 700 and 900 cm^{-1} in the spectra of Figure 6 arise from aromatic C-H out-of-plane deformation. The position of each peak denotes the number of adjacent ring hydrogen atoms; 830-900 cm^{-1} , one lone H atom; 800-860 cm^{-1} , two adjacent H atoms; 735-820 cm^{-1} , three to five adjacent H atoms (40,48). Figure 8 portrays the variation in distribution of aromatic hydrogen for the six samples analyzed. Although selective removal of PAC with substituents at certain positions would have some influence on the distribution of aromatic H atoms, one might expect the overall loss of substituted PAC to cause a general shift toward a higher number of adjacent H atoms. Figure 8 displays a slight decrease in the fraction of lone H--more pronounced in Regime 1 ($8.7 > Y > 4.5$)--that could be considered consistent with the loss of substituted PAC. Less amenable to explanation, however, is the increase in two adjacent H at the expense of the three adjacent H in Regime 2 ($Y < 4.5$)--a sign, perhaps, that other factors are also at work, e.g., destruction of heterocyclic structures and ring build-up processes that can form PAC of larger ring number and a higher degree of peri-condensation. Figure 8 allows no conclusions to be drawn about the relative reactivities of different positional isomers of substituted PAC.

EXTENSION: IMPLICATIONS FOR SOOT FORMATION

The conversion of PAC to soot can be approximated by the following scheme:



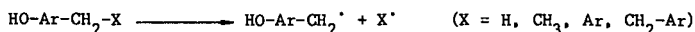
where the three reactions are depicted as irreversible since our experiments never show a net production of substituted PAC or a net destruction of soot. Although many uncertainties remain about the relative dominance of the three reactions, the data imply the following about this network:

- 1) In both Regimes, at least one of either R2 or R1-R3 must occur.
- 2) R3 must occur in Regime 2. It occurs in Regime 1 only if $\text{R1} = \text{R3}$.
- 3) If soot forms via the combination R1-R3, then $\text{R1} = \text{R3}$ in Regime 1 and $\text{R1} < \text{R3}$ in Regime 2.
- 4) If soot cannot form via the combination R1-R3, then R2 must occur throughout Regimes 1 and 2; and R3 must occur only in Regime 2.

It would appear that if conversion of substituted PAC to soot does first entail conversion to unsubstituted PAC, then it does not merely involve removal of the substituent group: Lewis and Edstrom (38) report 7,12-dimethylbenz[a]-anthracene to form significantly more soot than benz[a]anthracene. Davis and Scully (10) and Glassman (16) report the alkylated naphthalenes and benzenes to have higher sooting tendencies than their unalkylated homologs. If benzene, naphthalene, and benz[a]anthracene are less likely to form soot than their alkylated derivatives, then it is unlikely that conversion of an alkylated PAC to soot proceeds via the removal of the alkyl group to form the unalkylated homolog.

If, as asserted by others (20,24,37), the conversion of PAC to soot involves the formation of a reactive free radical, then PAC reactivity should correlate with the ease of radical formation. The formation of a σ -type radical (e.g., phenyl, naphthyl) by abstraction of a ring-attached H atom or methyl group requires approximately 100 kcal/mole (37)--a high bond dissociation energy due to the localization of the resulting free electron. To form π -type radicals like benzyl, however, requires only about 77 kcal/mole because the resulting unpaired electron is resonance-stabilized (37). Alkyl-substituted PAC would then be expected to be more reactive than unalkylated PAC.

Substituted PAC with hydroxyl groups can evidently form radicals even more easily. Gavalas (15) reports the profound activating effect of a hydroxyl group substituted in the *ortho* or *para* position of an aromatic unit (Ar) linked by a methylene bridge. Because of keto-enol tautomerism, dissociations of the type



are very highly energetically favored over the type



Activation energies for the dissociation of aryl and aryl/alkyl ethers lie in the same range as those of aromatics with alkyl substituents or methylene bridges (15). Thus our experimentally observed order of depletion of PAC parallels that suggested by ease of radical formation: hydroxyl-substituted PAC > alkyl- and ether- substituted PAC > unsubstituted PAC.

CONCLUSIONS

1. As observed in previous studies in our laboratory (42), there is a constancy of summed PAC and soot yields that indicates a conversion of PAC to soot.
2. The ability to separate substituted PAC from unsubstituted PAC reveals differences in their pyrolysis behaviors: At low temperatures (< 1312 K at 6 in) or short times (drop distances < 4 in at 1375 K), yields of substituted PAC fall markedly with an increase in either temperature or time; yields of unsubstituted PAC remain constant. Both classes of PAC react away, however, at higher temperatures or longer times.
3. Plotting substituted and unsubstituted PAC yields versus total PAC yield Y reconciles data taken at constant distance and variable temperature with those taken at constant temperature and variable distance. Because substituted and unsubstituted PAC yields prove to be solely functions of Y , Y aptly serves as a single parameter for pyrolysis severity since it accounts for variations in composition due to either temperature or time.

4. For the bituminous coal investigated, the yields of substituted and unsubstituted PAC suggest two PAC conversion regimes. Although reactivities may vary from species to species within a class, at low PAC conversions, substituted PAC as a class clearly display a much higher decay than the unsubstituted PAC: Substituted PAC yields fall by a factor of ~3.5; whereas the unsubstituted PAC show no net change. Though still evident at high PAC conversion, differences in the two classes' decays are much less pronounced. Unsubstituted PAC yields remain appreciably above those of the substituted PAC, but both classes undergo significant conversion to soot.
5. Conversion of PAC corresponds to differences in the kinds of functional groups present. At high values of Y, FT-IR shows that there are significant amounts of PAC with alkyl, ether, carbonyl, and hydroxyl and/or amino groups. Further pyrolysis, however, effects selective removal of the hydroxyl- and/or amino-substituted PAC. As the unsubstituted PAC become more prevalent, relative contributions from alkyl and ether functionalities go down and carbonyl substitution becomes slightly more significant.
6. Without specifying the kind of reaction mechanism, we can apply frontier orbital theory to PAC conversion reactions. This theory, along with values of ionization potentials found in the literature (12), suggests that PAC reactivity follows the order:
 aromatic amines > aromatic ethers \approx multialkylated PAC \approx phenols >
 monoalkylated PAC > unsubstituted PAC > carbonyl-substituted PAC,
 which is consistent with our experimental results.
7. If we restrict the PAC conversion reactions to involve free radical formation, then we again see agreement between theory and experiment. Less energy is needed to form free radicals from PAC with hydroxyl, alkyl, and ether substituents than from unsubstituted PAC.

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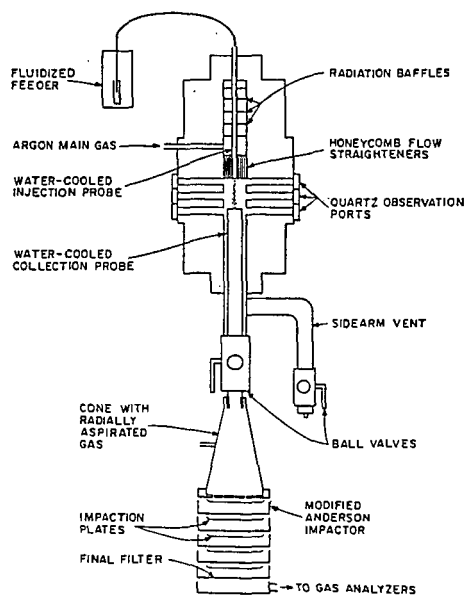


FIGURE 1: THE PYROLYSIS FURNACE AND COLLECTION SYSTEM

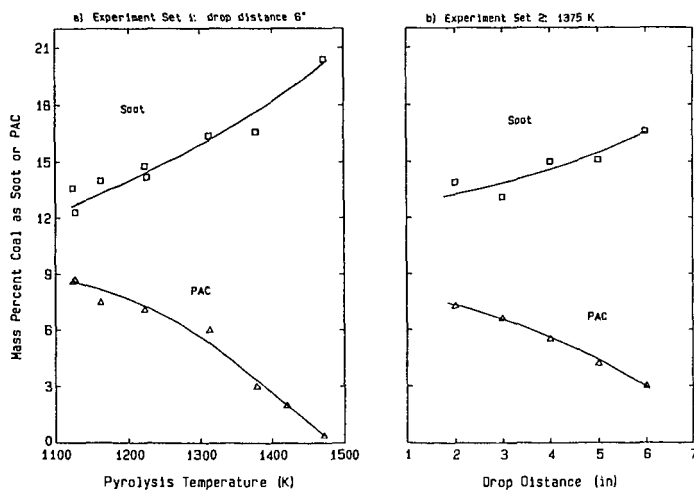


FIGURE 2: SOOT AND PAC YIELDS AT VARIOUS PYROLYSIS CONDITIONS

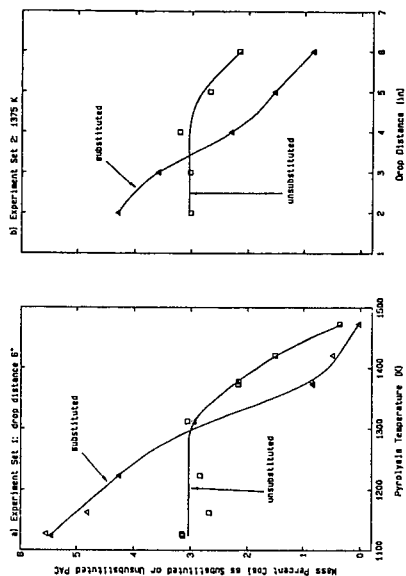
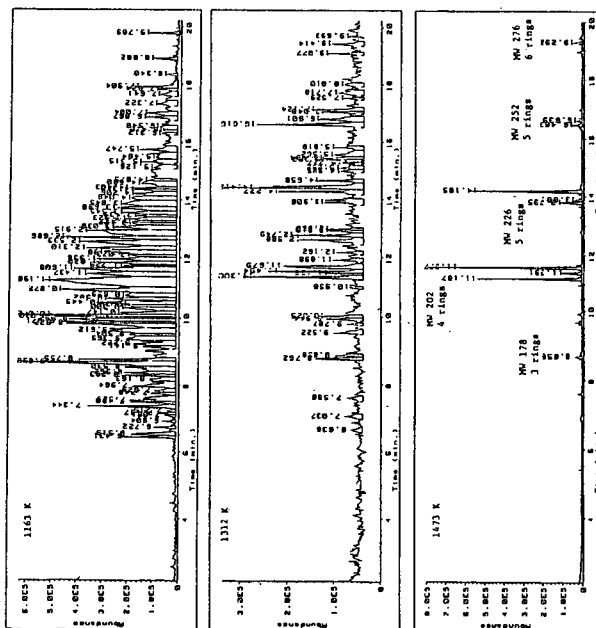


FIGURE 4: YIELDS OF SUBSTITUTED AND UNSUBSTITUTED PAC

FIGURE 3: PAC TOTAL ION CHROMATOGRAMS FOR THREE PYROLYSIS TEMPERATURES

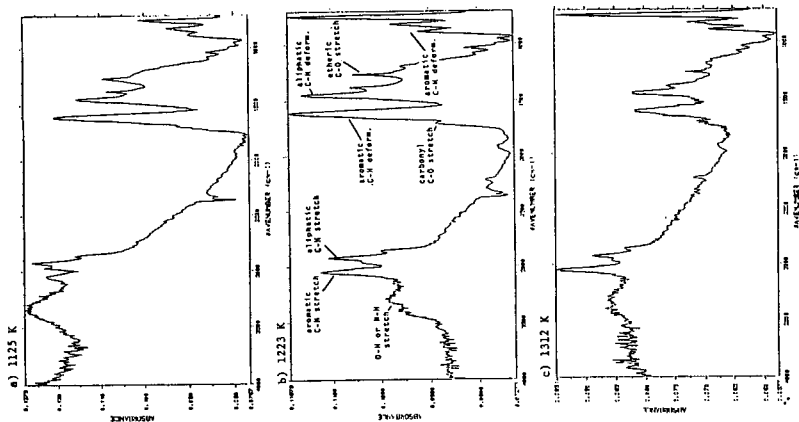


FIGURE 8: FT-IR SPECTRA OF PAC FOR THREE PYROLYSIS TEMPERATURES

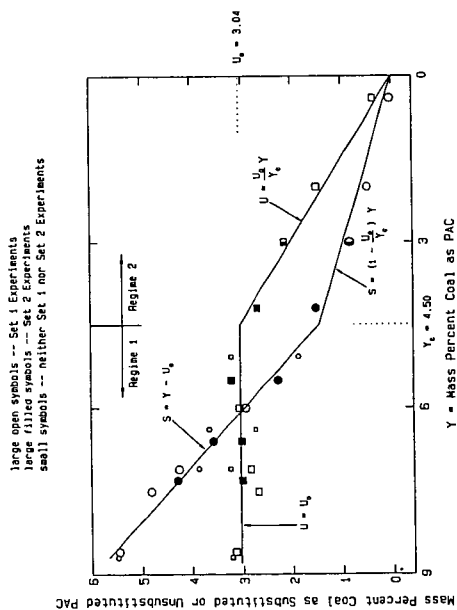


FIGURE 5: SUBSTITUTED AND UNSUBSTITUTED PAC YIELDS VERSUS TOTAL PAC YIELD

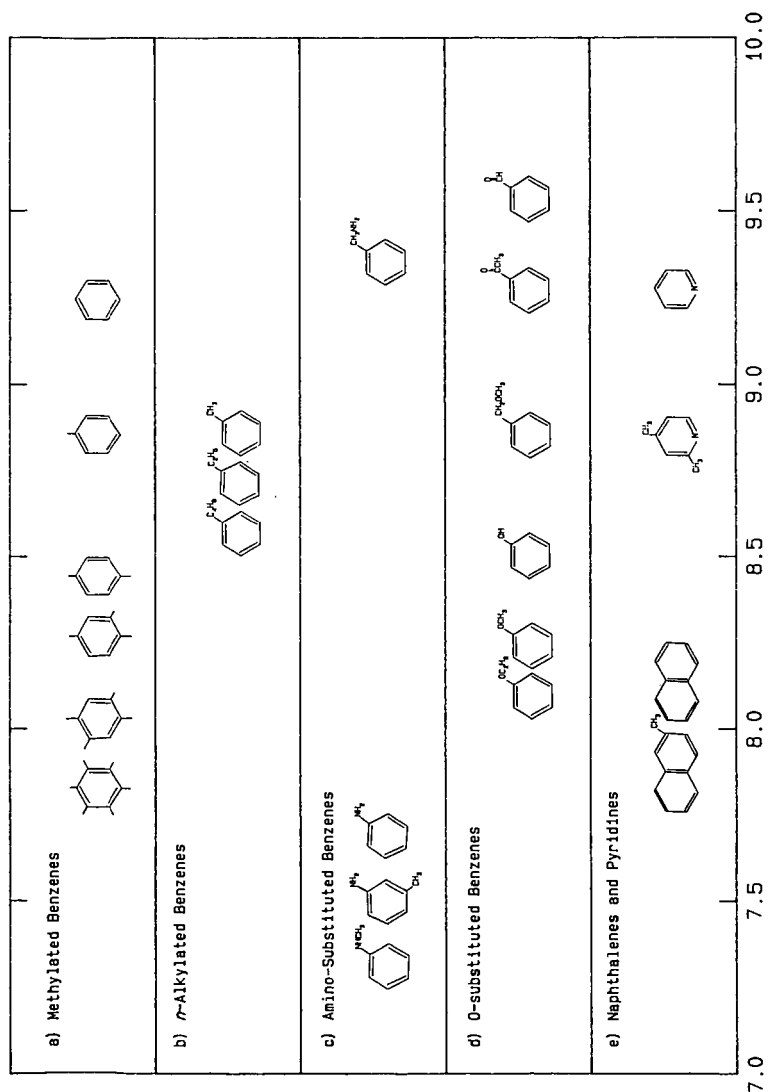


FIGURE 7: IONIZATION POTENTIALS (eV) OF AROMATICS
from Franklin, *et al.* (12)

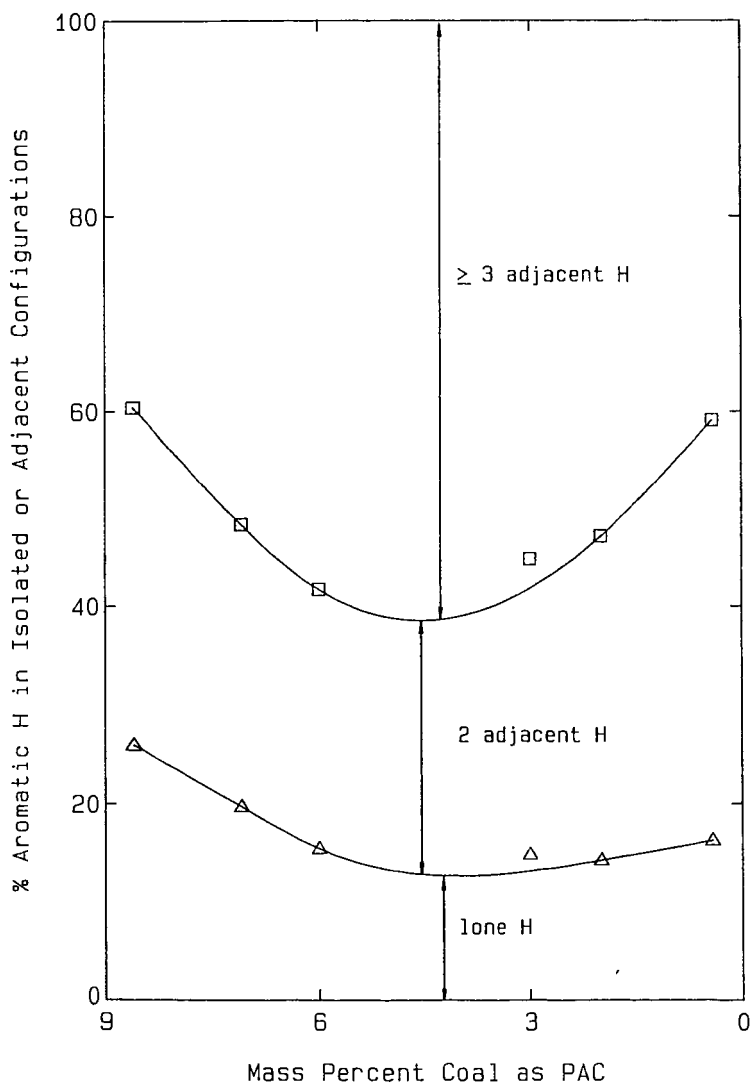


FIGURE 8: VARIATION IN AROMATIC H ADJACENCY FROM FT-IR